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SOLID COMPLEXES FROM MANDELOHYDROXAMIC ACID AND SEVERAL DIVALENT METALLIC CATIONS: A THERMAL AND SPECTROSCOPIC STUDY

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ABSTRACT

Solid crystalline complexes of mandelohydroxamic acid (MHA) and 12 metallic divalent cations have been obtained and characterized The determined stoichiometries are 2 (MHA) 1 (cation) for Mg(II), Ca(II), Sr(II), Ba(II), Mn(II), Co(II), Ni(II), Zn(II), Cd(II), Cu(II) and Pb(II) and 1 1 for Hg(II) The different water contents were measured and the thermal behaviour was studied by TG, CDS and IR spectrophotometric techniques

INTRODUCTION

The ability of hydroxamic acids to form complexes with metallic cations has been extensively studied [1–3], however, there are only a few papers which describe the thermal behaviour and stability of such complexing agents and their complexes in the solid state [4–7]

Hydroxamic acids generally form complexes of stoichiometry 2 1 with divalent cations in neutral media, except in cases such as 5,5′-methylene-di-salicylhydroxamic and 5,5′-dithio-disalicylhydroxamic acids, which lead to different stoichiometries [8,9]

Our purpose in this work is the synthesis of complexes derived from mandelohydroxamic acid (MHA) and divalent metallic cations, and to investigate the thermal behaviour of these solids by means of TGA–DTG, CDS and IR spectroscopic techniques

EXPERIMENTAL

Materials

MHA was synthesized following the method described by Hauser and Renfrow [10] The isolated acid was recrystallized in petroleum ether methanol 2 1

All the MHA–divalent cation complexes were prepared in this general way over 10 cm^3 of a hot solution of 0 5 M MHA (as potassium salt), 10 cm^3 of 0 1 M solution of the corresponding metallic salts were added with stirring The precipitate was immediately filtered off, washed with cold water and dried over calcium carbonate Analytical data are shown in Table 1

Apparatus

Elemental analyses were carried out at the Institute of Bio-organic Chemistry of Bàrcelona

Thermal studies were carried out on a Mettler TA 3000 System provided with a Mettler TG 50 thermobalance and a Mettler differential scanning calorimeter TG curves were obtained at a heating rate of 10 ° C min^{-1} in a static air atmosphere, using samples of weights between 5 81 and 11 61 mg The temperature range studied was 40–1000 ° C in some cases and 40–800 ° C in others The DSC curves were registered at a heating rate of 10 ° C min^{-1} in a static atmosphere of air within the range 30–600 ° C The sample weights varied from 1 24 to 1 71 mg in these cases

TABLE 1

Elemental analysis data

Compound	C (%)		H (%)		N (%)		H_2O (%) [a]	
	Calc	Found	Calc	Found	Calc	Found	Calc	Found
MHA	57 48	57 46	5 38	5 37	8 38	8 40		
$Mg(MHA)_2\ 2H_2O$	48 90	47 84	5 09	5 10	7 13	7 13	9 20	14 06
$Ca(MHA)_2\ 2H_2O$	47 04	48 00	4 90	4 66	6 86	6 95	8 82	16 82
$Sr(MHA)_2\ H_2O$	43 87	42 74	4 11	4 15	6 39	6 16	4 10	10 35
$Ba(MHA)_2\ 2H_2O$	38 02	37 98	4 04	3 95	5 48	5 54	7 12	7 11
$Mn(MHA)_2\ 2H_2O$	45 59	45 60	4 75	4 71	6 65	6 64	8 51	8 64
$Co(MHA)_2\ 1/2H_2O$	48 00	47 20	4 20	4 13	7 00	6 43	2 20	2 40
$Ni(MHA)_2\ 2H_2O$	45 00	44 51	4 20	4 12	6 50	6 33	8 43	8 32
$Zn(MHA)_2\ 2H_2O$	44 30	44 67	4 62	4 55	6 46	6 33	8 31	12 72
$Cd(MHA)_2\ 2H_2O$	39 96	39 58	4 16	4 17	5 82	5 72	7 49	7 36
$Cu(MHA)_2$	48 50	47 01	4 04	4 34	7 08	6 61		
$Pb(MHA)_2$	35 59	35 69	2 96	2 84	5 19	5 20		
Hg(MHA)	26 18	26 76	2 18	1 86	3 82	3 78		

[a] Water percentages measured from TG data

IR spectra were produced on a Perkin Elmer 297 spectrophotometer as KBr pellets prepared with the solids just obtained and after 1 h heating at 25, 80 and 150 °C

RESULTS AND DISCUSSION

The solid MHA–metal complexes prepared in the specified experimental conditions have a stoichiometry of 2 1 for all cations except Hg(II) which forms a 1 · 1 complex The complexes obtained from Pb(II), Hg(II) and Cu(II) as well as MHA itself and its potassium salt crystallize without water of crystallization or coordination (Table 1)

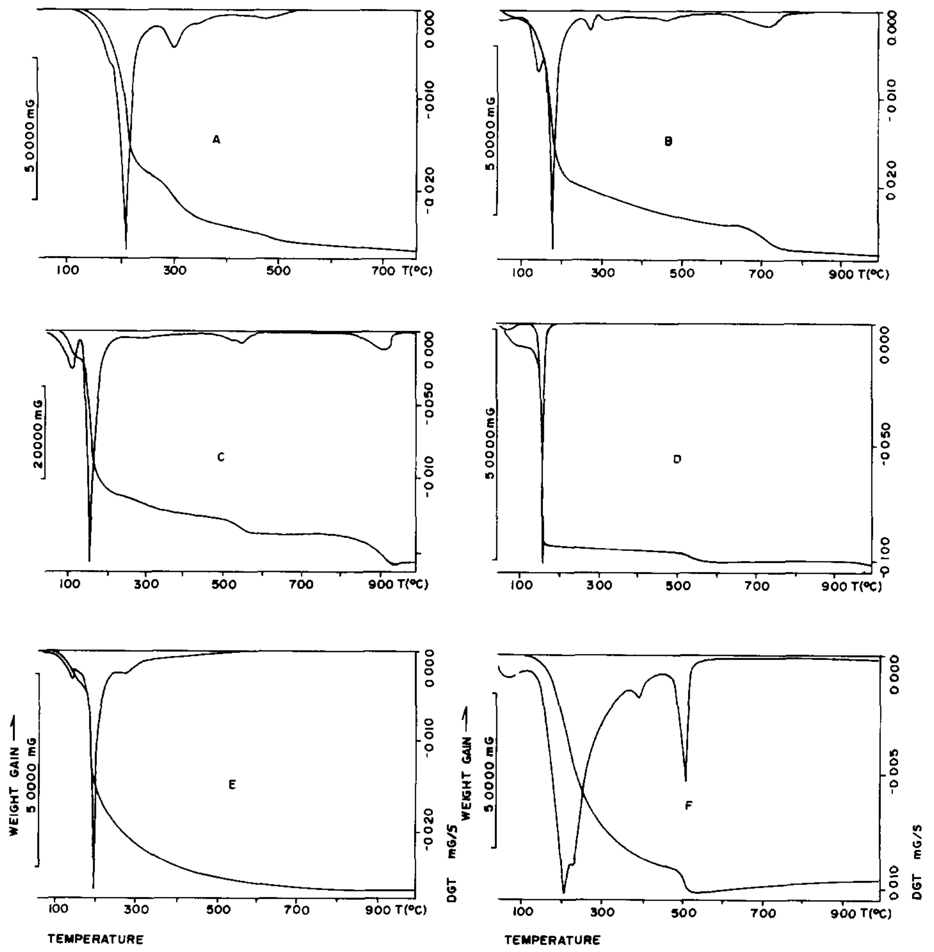


Fig 1 Thermogravimetric curves of mandelohydroxamic acid complexes of (A) Mg(II), (B) Ca(II), (C) Sr(II), (D) Ba(II), (E) Mn(II), (F) Co(II), (G) Ni(II), (H) Zn(II), (I) Cd(II), (J) Cu(II), (K) Pb(II), (L) Hg(II) and mandelohydroxamic acid (M)

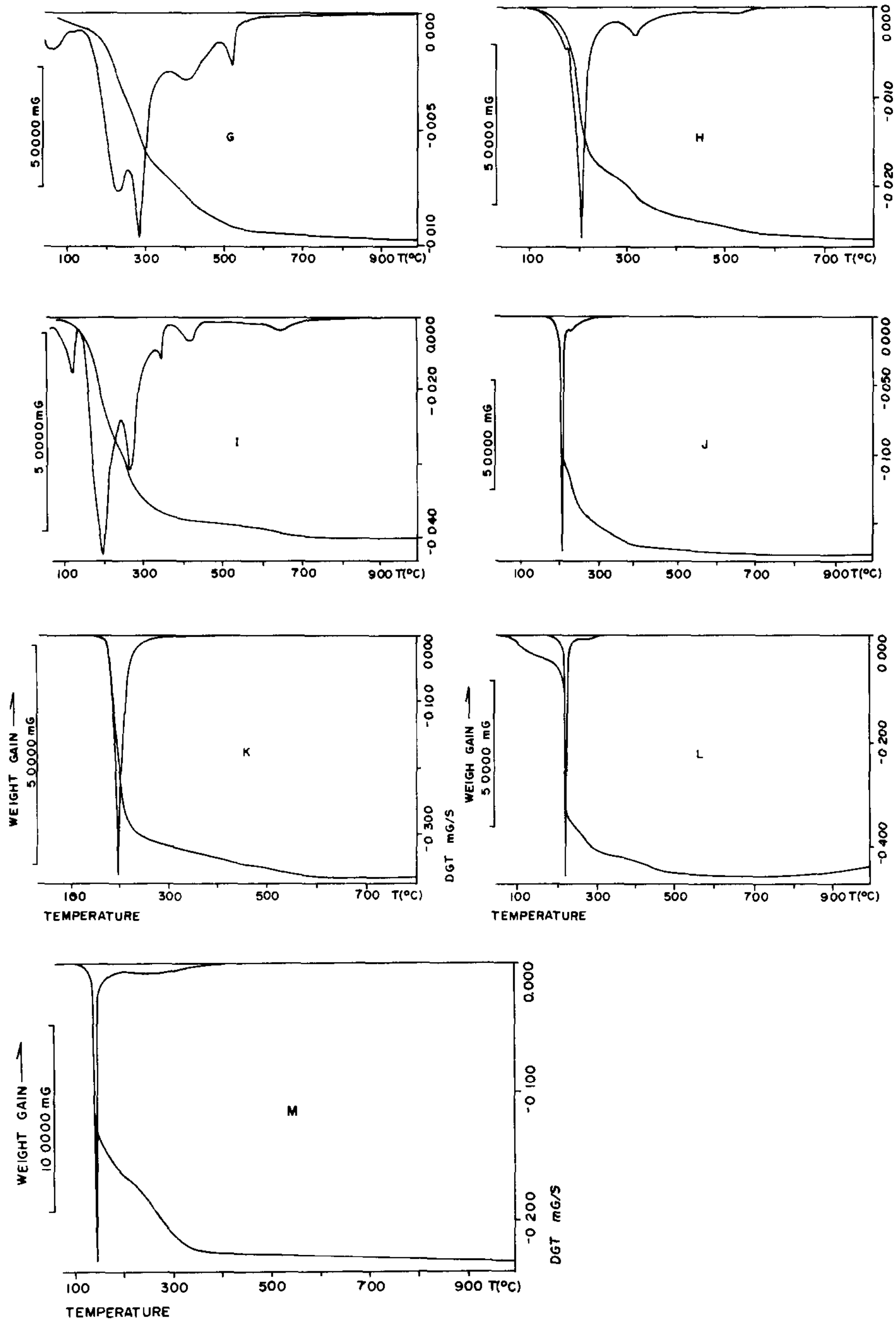


Fig 1 (continued)

Hydrated complexes undergo a dehydration process between 40 and 140 °C (Fig 1), and in the compounds from Mg(II), Ca(II), Sr(II) and Zn(II) this process overlaps with the pyrolysis, the mass loss in such

TABLE 2

TG assignations for dehydration processes

Process		Weight loss (%)		Temperature range (° C)
		Calc	Found	
$Mg(MHA)_2\ 2H_2O$	$\rightarrow Mg(MHA)_2$	9 20	14 06	100–185
$Ca(MHA)_2\ 2H_2O$	$\rightarrow Ca(MHA)_2\ H_2O$	4 41	4 42	40–120
$Ca(MHA)_2\ H_2O$	$\rightarrow Ca(MHA)_2$	4 41	12 40	120–165
$Sr(MHA)_2\ H_2O$	$\rightarrow Sr(MHA)_2$	4 10	10 35	40–130
$Ba(MHA)_2\ 2H_2O$	$\rightarrow Ba(MHA)_2$	7.12	7 11	40– 90
$Mn(MHA)_2\ 2H_2O$	$\rightarrow Mn(MHA)_2$	8 51	8 64	60–140
$Co(MHA)_2\ 1/2H_2O$	$\rightarrow Co(MHA)_2$	2 20	2 40	60–140
$Ni(MHA)_2\ 2H_2O$	$\rightarrow Ni(MHA)_2$	8 43	8 32	40–140
$Zn(MHA)_2\ 2H_2O$	$\rightarrow Zn(MHA)_2$	8 31	12 72	100–185
$Cd(MHA)_2\ 2H_2O$	$\rightarrow Cd(MHA)_2$	7 49	7 36	40–140

complexes being greater than that corresponding to the loss of water only In the other compounds the percentages of mass loss are in good agreement with the calculated values Only in the Ca(II) derivative can different hydration states be distinguished (see Table 2)

Dehydration is accompanied, as expected, by an endothermic peak in CDS curves (Table 3), the involved energies being of 108 4 and 126 1 kJ mol^{-1} for the complexes of Mg and Zn

In the complexes of alkaline-earth cations an inverse proportionality between dehydration temperature and ionic radius can be noted (see Table 2)

Anhydrous complexes are stable within a short temperature range, undergoing a strong decomposition in two or more steps as can be seen in Table 4, where the different temperatures corresponding to mass losses and the experimental and calculated residues (as percentages) are shown for the assigned decomposition processes MHA (and its potassium salt) decomposes in a similar way the first step (about 180 ° C) corresponds generally to the greatest loss of mass (60%) and total decomposition occurs below 500 ° C Most of the anhydrous compounds show a detectable stage at higher

TABLE 3

CDS data [a]

Compound	T_1	H_1	T_2	H_2	T_3	H_3
$Zn(MHA)_2\ 2H_2O$	163	126 1	186	−45 4	276	−61 4
$Mg(MHA)_2\ 2H_2O$	162	108 4	193	−46 8	270	−55 6
$Pb(MHA)_2$	178	−111 2	192	−95 4		
Hg(MHA)			200	−142 7		

[a] T_i are given in ° C and H_i in kJ mol^{-1}

TABLE 4

TG assignations for the pyrolysis processes

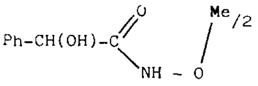
Process	Temperatures (° C)	Residue (%)		T*
		Calc	Found	
Mg(MHA)$_2$ → MgCO$_3$	195, 300	21 41	19 82	
MgCO$_3$ → MgO	510	10 27	10 35	800
Ca(MHA)$_2$ → CaCO$_3$	165, 280, 420	24 50	23 82	
CaCO$_3$ → CaO	680	13 75	13 93	950
Sr(MHA)$_2$ → SrCO$_3$	140, 260, 500	35 37	33 77	
SrCO$_3$ → SrO	880	23 67	23 81	950
Ba(MHA)$_2$ → BaO	140, 520	30 34	30 02	800
Mn(MHA)$_2$ → MnO	160, 262, 480	16 77	16 85	950
Co(MHA)$_2$ → CoCO$_3$	170, 262, 375	29 75	26 18	
CoCO$_3$ → CoO	485	18 72	18 52	520
CoO → Co$_3$O$_4$		20 06	20 71	950
Ni(MHA)$_2$ → NiCO$_3$	180, 262, 370	27 82	25 30	
NiCO$_3$ → NiO	530	17 55	17 81	950
Pb(MHA)$_2$ → PbO	180, 420, 530	41 39	41 40	800
Zn(MHA)$_2$ → ZnO	185, 310, 500	18 77	17 81	800
Cd(MHA)$_2$ → CdCO$_3$	160, 265, 410	35 88	33 39	
CdCO$_3$ → CdO	620	26 72	27 31	950
HgMHA → pyrolysis	160, 265, 410			
Cu(MHA)$_2$ → CuCO$_3$	221	31 20	30 73	
CuCO$_3$ → CuO	450	24 91	23 10	800

T*, temperature at which the residues were measured

temperatures in which the corresponding carbonate seems to be formed before total oxidation, and the measured percentages of residual masses are in good agreement with the calculated values

The complexes derived from Cu(II), Zn(II), Ni(II), Co(II) and Mn(II) follow the thermal stability order proposed by Irving and Williams [11] Mn < Co < Ni < Cu > Zn

IR data are shown in Table 5, where a shift of the C=O stretching band (1660 cm^{-1} for free MHA) to lower wavelengths (80–30 cm^{-1}) occurs and simultaneously there is a shift toward higher wavenumbers (about 40–30 cm^{-1}) in the C–N bending band in all the solid complexes while the N–H stretching absorption is shifted in a similar way, although these variations are not as large as those of complexes in which N–H bond is directly involved [12] The rest of bands seems to remain unaffected and all the data agree with the formula



in which a partial loss of double bond character due to the participation of the carbonyl group in the chelation (and also due to a certain double bond

TABLE 5

IR absorption bands (cm^{-1})

Compound	O–H		N–H		C=O		N–H		C–N		N–O			
	20 °C	150 °C	20 °C	150 °C	20 °C	150 °C	20 °C	150 °C	20 °C	150 °C	20 °C		150 °C	
MHA	3440b	3440b	3280	3280	1660	1720	1535	–	1343	–	1023	975	1023	–
K–MHA	–	–	3260	3480	1630	–	1535	1535	1310	1310	1010	–	–	–
$(MHA)_2Mg\ 2H_2O$	3450b	3450b	3232	–	1619	1619w	1554	–	1382	–	1032	994	–	–
$(MHA)_2Ca\ 2H_2O$	3400b	–	3210b	–	1630	–	1515	–	1382	–	–	989	–	–
$(MHA)_2Sr\ H_2O$	3520b	–	3265	–	1630	–	1545	–	1342	–	1020	980	–	–
$(MHA)_2Ba\ 2H_2O$	3500b	–	3248	–	1632	–	–	–	1386	–	1025	985	–	–
$(MHA)_2Co\ 1/2H_2O$	3500b	–	3200b	–	1612	–	1515	–	1380	–	1030	985	–	–
$(MHA)_2Ni\ 2H_2O$	3400b	3400b	3200b	3200b	1615	1615	1512	1512	1385	1385	1030	985	1030	985
$(MHA)_2Zn\ 2H_2O$	3460b	3460b	3235	3235	1620	1620	1555	1555	1383	1383	1032	993	1032	993
$(MHA)_2Pb$	–	–	3212	–	1605	–	1518	–	1383	–	1028	985	–	–
$(MHA)_2Cd\ 2H_2O$	3450b	–	3225	–	1612	–	1545	–	1382	–	1010	987	–	–
$(MHA)_2Cu$	–	–	3200b	3200b	1580	1580	–	–	1369	1369	1026	–	1026	–
$(MHA)Hg$	–	–	–	–	–	–	–	–	1390	–	1008	990	–	–

K–MHA, potassium mandelohydroxamate

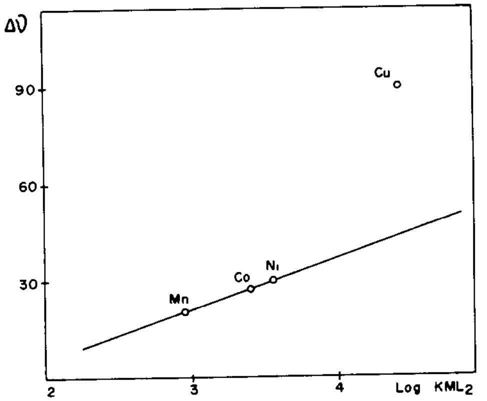
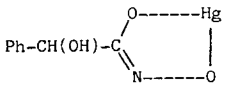


Fig 2 Relationship between $\Delta\nu$ (νC=O band shifts of the complexes in comparison to free ligand) and log K_{ML_2} regarding the Mn, Co, Ni and Cu complexes

character of the C–N linkage as a result of electron withdrawing effects) justifies the measured shifts [13,14]

A single exception among the compounds studied is the MHA–Hg(II) complex with 1 1 stoichiometry the carbonyl band has been changed for a new absorption (1528 cm^{-1}) that has been assigned to a C=N stretching band So a different formula has to be written for this 1 1 complex



Most absorption bands are strongly affected by temperature In consequence the whole spectrum changes, and the bands disappear or become such weaker after heating for 1 h at 150 °C in all the complexes studied, except in the Ni, Zn and Cu compounds In the potassium salt a new sharp band appears after 1 h heating at 150 °C, around 2160 cm^{-1}, corresponding to a O=C=N– group [14,15]

Dehydration processes were also detected by comparing the spectra obtained at different temperatures

A linear relationship between stability constants [16] and the shift of the C=O band could be found in the Mn, Co and Ni complexes (Fig 2)

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